

# Introduction to Polymers

## Second Edition

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## ATTACHMENT A



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The side reactions lead to loss of initiator, termination of chain growth and formation of polymers with broad molar mass distributions. For methyl methacrylate ( $R = R_1 = \text{CH}_3$ ) the side reactions essentially can be eliminated by using polar solvents, low temperatures, bulky initiators (for which reaction with the  $\text{C}=\text{O}$  group is sterically-hindered) and large counter-ions, e.g. by polymerization in tetrahydrofuran at  $-75^\circ\text{C}$  using cumylcations as initiator.

The ability to produce polymers of well-defined structure using anionic polymerization is of great importance and despite the above difficulties it is widely used for this purpose. Thus polymers with narrow molar mass distributions, terminally-functionalized polymers, and perhaps most important of all, well-defined block copolymers (Section 2.16.9) can be prepared using anionic polymerization.

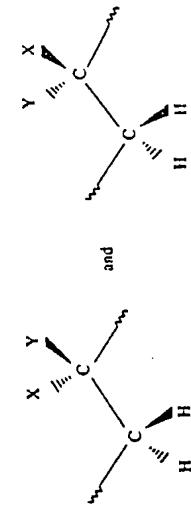
## 2.8 Stereochemistry of polymerization

In addition to the effects of skeletal structure and of the chemical composition of the repeat units, the properties of a polymer are strongly influenced by its molecular microstructure. Variations in the geometric and configurational arrangements of the atoms in the repeat unit, and the distribution of these different spatial arrangements for the repeat units along the chain, are of particular importance.

Different molecular microstructures arise from there being several possible modes of propagation. The possibility of head-to-tail and head-to-head placements of the repeat units has been encountered already, with the observation that for both steric and energetics reasons the placement is almost exclusively head-to-tail for most polymers. Therefore in the subsequent sections dealing with the stereochemistry of propagation only head-to-tail placements will be considered.

### 2.8.1 Tacticity

For polymers prepared from monomers of the general structure  $\text{CH}_2 = \text{CXY}$ , where X and Y are two different substituent groups, there are two distinct configurational arrangements of the repeat unit.



where  $\text{V}$  and  $\text{V}^\circ$  indicate bonds which are extending above and below the plane of the paper respectively. These two stereoisomers of the repeat unit cannot be interchanged by bond rotation and exist because the substituted carbon atom is attached to four different groups (i.e. it is asymmetric). Unlike simple organic compounds with asymmetric carbon atoms, the stereoisomers indicated above show no significant optical activity because the two polymer chain residues attached to the asymmetric carbon atom are almost identical. Nevertheless, the existence of two isomeric forms of the repeat unit, and in particular their distribution along the polymer chain, are of great significance. In *isotactic* polymers all the repeat units have the same configuration, whereas in *syndiotactic* polymers the configuration alternates from one repeat unit to the next. *Atactic* polymers have a random placement of the two configurations. These three stereochemical forms are shown for short segments of polymer chains in

Fig. 2.9

Polypropylene ( $X = \text{H}$ ,  $Y = \text{CH}_3$ ) provides a good example of the importance of tacticity. The commercial material is essentially isotactic and

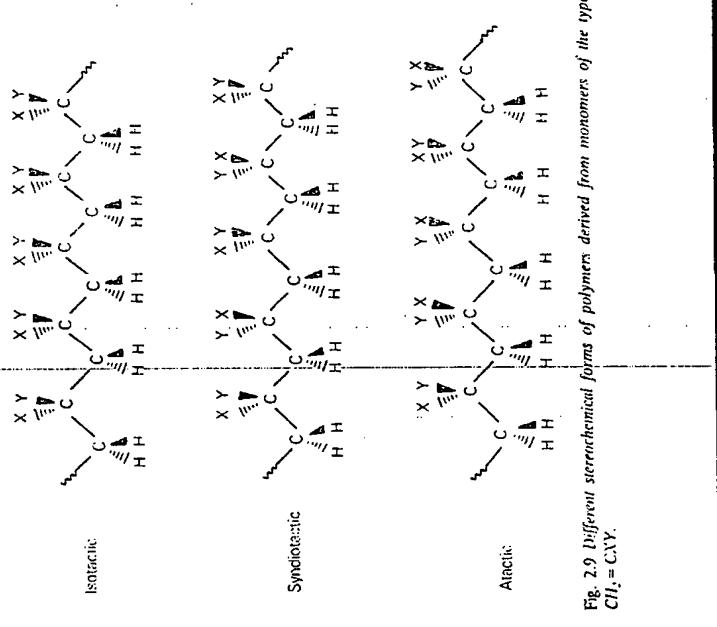


Fig. 2.9 Different stereochemical forms of polymers derived from monomers of the type  $\text{CH}_2 = \text{CXY}$ .

due to its regular structure is crystalline (c. 65%). It is the crystalline regions that give rise to the good mechanical properties of commercial polypropylene. In contrast, atactic polypropylene is unable to crystallize because of its irregular structure and is a soft, wax-like amorphous material which has no useful mechanical properties.

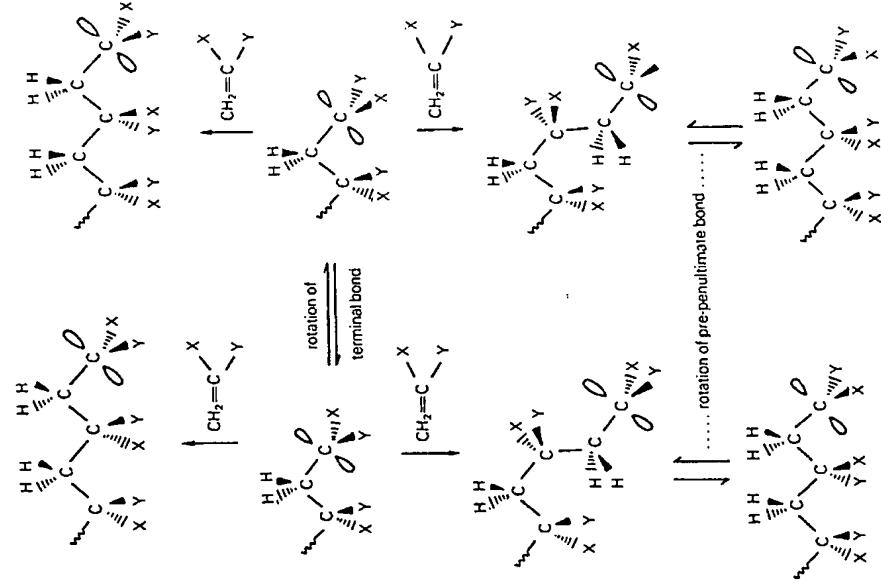


Fig. 2.10 Elementary features of the stereochemistry of propagation.

The tacticity of a polymer is controlled by the stereochemistry of propagation, some elementary aspects of which are illustrated in Fig. 2.10. The terminal active centres of propagating chains in free-radical, cationic and anionic polymerizations can be considered to be  $sp^2$  hybridized, the remaining p-orbital containing one, none and two electrons respectively. This form of hybridization is normal for free radicals and carbocations, but for catiionic active centres is a consequence of resonance with the substituent group(s) (a requirement for which is coplanarity and a change from the normal  $sp^3$  to  $sp^2$  hybridization). Thus in each case there is a planar arrangement of the groups about the terminal active carbon atom and so its configuration in the resulting polymer molecule is determined by the way in which monomer adds to it in a propagation step. As indicated in Fig. 2.10, the orientation of the substituent groups on the terminal active carbon atom relative to the orientation of those on the asymmetric carbon atom of the penultimate repeat unit, and the face of the planar active centre to which the molecule of monomer adds, are of great importance. Usually, steric and/or electronic repulsion between similar substituent groups results in a slight preference for syndiotactic rather than isotactic placements. This preference is accentuated by reducing the reaction temperature and highly syndiotactic polymers can be formed by ionic polymerization in a polar solvent at low temperature (e.g. anionic polymerization of methyl methacrylate initiated by 9-fluorenyllithium at  $-78^\circ\text{C}$  in tetrahydrofuran). In contrast, the relatively high temperatures normally employed for free-radical polymerizations result in the formation of essentially atactic polymers.

Highly isotactic polymers can be prepared by ionic polymerization if there is strong coordination of the counter-ion with the terminal units in the polymer chain and with the incoming molecule of monomer. However, this is difficult to achieve with non-polar monomers and usually requires the monomer to have polar substituent groups which can act as sites for strong coordination (e.g. cationic polymerization: vinyl ethers; anionic polymerization: methacrylate esters). In order to prepare highly isotactic polymers from such polar monomers the reaction must be carried out at low temperature in a non-polar solvent using an initiator which yields a small counter-ion so that ion-pair association is promoted (e.g. solvent: toluene at  $-78^\circ\text{C}$ ; cationic initiator: boron trifluoride etherate; anionic initiator: 1,1-diphenylhexyl lithium). The coordination is easily disrupted (e.g. by addition of a small quantity of a polar solvent) resulting in loss of the stereochemical control and formation of predominantly syndiotactic polymer. Isotactic polymers are more easily prepared from non-polar monomers by polymerizations involving coordination to transition metals (Section 2.9).

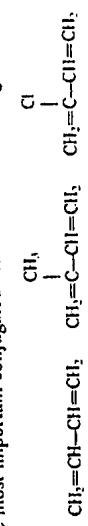
Polymers with more complex tacticities are formed from monomers of the general structure  $\text{XCH}=\text{CHY}$  since each backbone carbon atom

is asymmetric. However, since these monomers do not readily form homopolymers they will not be considered here.

The complications of tacticity are absent in polymers prepared from monomers of the type  $\text{CH}_2=\text{CX}_2$  because they contain no asymmetric backbone carbon atoms and therefore must be stereoregular.

### 2.8.2 Polymerization of conjugated dienes

The most important conjugated dienes are the following 1,3-dienes



which have the general structure  $\text{CH}_2=\text{CR}-\text{CH}=\text{CH}_2$ . There are four basic modes for addition of such 1,3-dienes to a growing polymer chain and these are shown in Table 2.10 (for butadiene there are only three modes because the 1,2- and 3,4-additions are identical since  $\text{R}=\text{H}$ ).

The importance of repeat unit isomerism in poly(1,3-dienes) is very clearly demonstrated by the naturally-occurring polysoprenes. *Gutta*

TABLE 2.10 Basic modes for addition of 1,3-dienes ( $\text{CH}_2=\text{CR}-\text{CH}=\text{CH}_2$ ) to a growing polymer chain ( $M_n^*$ )<sup>\*</sup>

Mode of addition	Product of addition	Repeat unit structure
1,2-addition	$\text{R}-\text{CH}_2-\overset{\bullet}{\text{C}}-\text{CH}_2$	$\text{R}-\text{CH}_2-\overset{\bullet}{\text{C}}-\text{CH}_2$
	$\text{CH}_2=\text{CH}_2$	$\text{CH}_2=\text{CH}_2$
3,4-addition	$\text{M}_n-\text{CH}_2-\overset{\bullet}{\text{C}}-\text{CH}_2$	$\text{M}_n-\text{CH}_2-\overset{\bullet}{\text{C}}-\text{CH}_2$
	$\text{CR}=\text{CH}_2$	$\text{CR}=\text{CH}_2$
cis-1,4-addition	$\text{M}_n-\text{CH}_2-\overset{\bullet}{\text{C}}=\text{C}-\text{CH}_2$	$\text{M}_n-\text{CH}_2-\overset{\bullet}{\text{C}}=\text{C}-\text{CH}_2$
	$\text{H} \quad \text{R}$	$\text{H} \quad \text{R}$
<i>trans</i> -1,4-addition	$\text{M}_n-\text{CH}_2-\overset{\bullet}{\text{C}}=\text{C}-\text{CH}_2$	$\text{M}_n-\text{CH}_2-\overset{\bullet}{\text{C}}=\text{C}-\text{CH}_2$
	$\text{H} \quad \text{CH}_2$	$\text{H} \quad \text{CH}_2$

\* For each mode there is the possibility of head-to-head or head-to-tail placement, and for 1,2- and 3,4-addition the additional complication of isotactic or syndiotactic placement.

*perdu* and *butata* are predominantly *trans*-1,4-polysoprene, and due to their regular structure are able to crystallize which causes them to be hard rigid materials. However, *natural rubber* is *cis*-1,4-polysoprene, which has a less symmetrical structure that does not allow easy crystallization under normal conditions and so is an amorphous rubbery material. The difference in regularity between these structures is shown schematically for chain segments containing four head-to-tail repeat units.

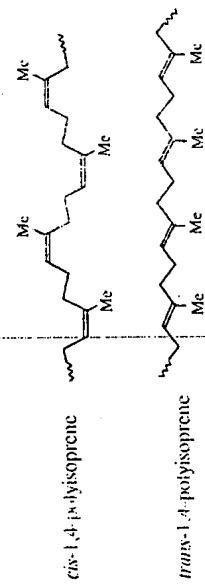
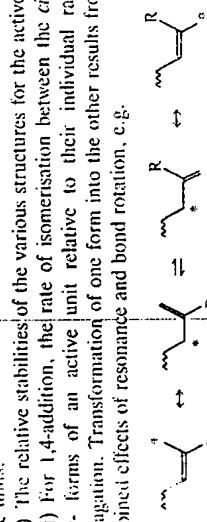


Table 2.11 shows the proportions of the different repeat units in homo-polymers of butadiene and isoprene prepared using various polymerization conditions. The factors which are of importance in determining these proportions are:

- The conformation of the 1,3-diene molecule when it adds to the growing chain since this is at least initially is retained in the new active unit formed by its addition. In the absence of specific effects, the molecules exist initially in the transoid conformation ( $\text{---}\text{C}=\text{C}\text{---}$ ) which is more stable than the cisoid ( $\text{---}\text{C}=\text{C}\text{---}$ ) and leads to a preponderance of initially *trans*-active units.
- The relative stabilities of the various structures for the active unit.
- For 1,4-addition, the rate of isomerisation between the *cis*- and *trans*-forms of an active unit relative to their individual rates of propagation. Transformation of one form into the other results from the combined effects of resonance and bond rotation, e.g.



where  $\ddot{\sigma}$  represents a single electron or a positive or negative charge.

In free-radical polymerization there are no special effects and the polymers obtained have a high proportion of *trans*-1,4 repeat units which increase in number at the expense of *cis*-1,4 repeat units as the reaction temperature is reduced. The preference for *trans*-1,4 addition is more pronounced for isoprene due to the presence of the methyl substituent group.